Rate of Hydrogen Atom Reaction with Ethanol, Ethanol-d_5, 2-Propanol, and 2-Propanol-d_7 in Aqueous Solution[†]

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Arrhenius parameters for the reaction of hydrogen atoms with ethanol, ethanol-d_5, 2-propanol, and 2-propanol-d_7 in aqueous solution have been determined by the use of pulse radiolysis and electron paramagnetic resonance free induction decay attenuation measurements. At 25.0 °C, the calculated rate constants for these compounds are $(2.04 \pm 0.06) \times 10^7$, $(2.77 \pm 0.26) \times 10^6$, $(1.01 \pm 0.07) \times 10^8$, and $(1.56 \pm 0.07) \times 10^7$ dm^3 mol^{-1} s^{-1}, respectively, with corresponding activation energies of 24.10 ± 0.50 (6.5−81.3 °C), 31.9 ± 1.2 (22.4−79.6 °C), 22.00 ± 0.26 (5.4−88.5 °C), and 27.45 ± 0.30 (5.7−86.5 °C) kJ mol^{-1}. The results of this study are compared to previous reports and ab initio calculations.

1. Introduction

Despite the importance of hydrogen atom reactions in the radiolysis of aqueous systems, particularly at low pH, to date there have been relatively few absolute rate constants measured for the reaction of hydrogen atoms with organic solutes. For the most part these have been determined using EPR techniques, with reaction rate constants calculated from analysis of the temporal behavior changes of the EPR $^\bullet$H atom signal upon the addition of solute.[1−16] For some systems, time-resolved measurements using optical monitoring of product formation or conductivity changes have also been possible. However, the bulk of the hydrogen atom rate constants tabulated in the compilations of Anbar et al.,[17] and Buxton et al.[18] have been deduced from indirect competition studies, by either steady state or pulsed electron techniques.

Many compounds have been used as competition kinetic standards for hydrogen atom reactions, one major group being the lower molecular weight aliphatic alcohols. These compounds undergo quantitative hydrogen atom abstraction[19] and have been used extensively to determine relative reaction rate constants for other solutes that do not produce molecular hydrogen upon $^\bullet$H atom reaction.[17−19] In radiolysis studies a correction for the fundamental yield of molecular hydrogen obtained from intraspur reactions is also required. A convenient variation has been the use of a deuterated alcohol as a standard, particularly 2-propanol-d_7, where the fundamental yield of atomic hydrogen is unambiguously determined from the HD product of abstraction.[17,18]

Of the many determinations of hydrogen atom reaction rate constants for these alcohols, almost all the measurements have been performed at room temperature. In a recent study, however, rate constants for the reaction of the hydrogen atom with methanol[5]

$$^\bullet\mathrm{H} + \mathrm{CH_3OH} \rightarrow \mathrm{H_2} + {}^\bullet\mathrm{CH_2OH} \qquad (1)$$

in aqueous solution were directly determined over a wide range of temperatures. Excellent Arrhenius behavior was obtained, with the measured values being well-described by the expression

$$\log_{10} k_1 = (11.64 \pm 0.17) - [(29\,400 \pm 800)/2.303RT] \qquad (2)$$

This paper reports an extension of the earlier study, with the direct measurement of rate constants and activation energies for the reaction of hydrogen atoms with the alcohols ethanol, ethanol-d_5, 2-propanol, and 2-propanol-d_7. Direct EPR detection of the change in the hydrogen atom concentration following pulse radiolysis was the monitoring method of choice[11,20] as conventional pulse radiolysis/optical transient absorption methodology is difficult to use given the weak absorption of product radicals at very short wavelengths. The pulsed EPR-based free induction decay (FID) attenuation method[6−8,21,22] was used as in the previous study because of the pseudo-first-order scavenging kinetics generally obtained.

2. Experimental Section

The procedure used for these experiments has been described in detail in several previous publications,[6−8,21,22] and thus only a brief description shall be given here. Hydrogen atoms were generated in aqueous solution within an EPR cavity by pulse radiolysis, using 3 MeV electrons from a Van de Graaff accelerator. Stock solutions were prepared by addition of $\mathrm{HClO_4}$ (Mallinkrodt, AR grade, 69.05%) or phosphate buffer (Baker, analyzed) to Millipore-filtered water. Exact acid concentrations were determined by calculation from standardization of the concentrated acid against 1.029 N HCl (Aldrich, Volumetric Standard). As the vapor pressures of these alcohols is high, no head space in the recirculating system could be tolerated; thus the system was completely filled with Ar-saturated stock solution (203.5 ± 1.0) mL and then sealed. The solution was flowed through a flat cell in the cavity at a rate sufficient to ensure that each cell volume was completely replaced between pulses. The actual volume irradiated in each pulse was less than 0.10 mL.

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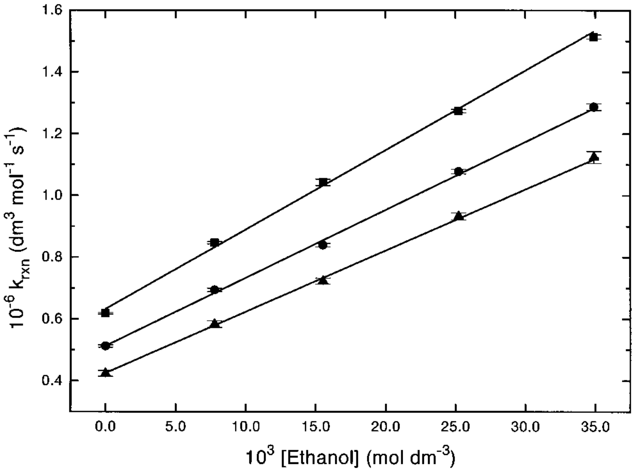

Figure 1. Dose dependence of the aqueous hydrogen atom scavenging rate constant determination for ethanol reaction at pH 2.0 and 22.0 °C using the Van de Graaff 55 (■), 25 (●), and 12 ns (▲) pulse widths. Solid lines are linear fits corresponding to calculated rate constants of (2.58 ± 0.02) × 10^7, (2.20 ± 0.02) × 10^7, and (2.01 ± 0.03) × 10^7 dm^3 mol^{-1} s^{-1}, respectively.

The approximate average radiation dose for this cell volume was 1.5, 3.0, and 7.0 krad/pulse for the 12, 25, and 55 ns pulses used, respectively. For extrapolation to obtain the limiting, zero-dose rate constants (see later), the relative dose values used were simply the average beam currents measured on a shutter positioned before the irradiation cell for the three pulse widths. These values were checked frequently to determine any small drift in the beam. A 35 ns microwave probe pulse was applied to the sample immediately after irradiation, and the resulting free induction decay of the $^{\bullet}$H atom low-field ($m_I = {}^1/_2$) EPR transition was recorded on a digital oscilloscope. Typically 500−2000 pulses were averaged to measure each FID, at a repetition rate of 120 Hz.

Scavenging experiments were performed by successive injection of the ethanol (MidWest Grain Products Co., USP, 99.5%), ethanol-d_6 (Aldrich, 99+% atom D), 2-propanol (Aldrich, HPLC grade, 99.5%), or 2-propanol-d_8 (Aldrich, 99+% atom D) which had also been saturated with argon. Accuracy of these concentrations is estimated at better than 2%.

All ab initio calculations were carried out using the SPARTAN molecular modeling program of Wavefunction, Inc.[23]

3. Results

$^{\bullet}$H Reaction with Ethanol. The overall hydrogen atom scavenging rate constant at pH 2.0 and 22.0 °C for the reaction

$$^{\bullet}H + CH_3CH_2OH \rightarrow H_2 + CH_3{}^{\bullet}CHOH \tag{3}$$

was determined at three different pulse widths (doses). These values are shown in Figure 1, with excellent linearity for these scavenging plots observed. The slopes of (2.01 ± 0.03) × 10^7, (2.20 ± 0.02) × 10^7, and (2.58 ± 0.02) × 10^7 dm^3 mol^{-1} s^{-1} for the 12, 25, and 55 ns pulses, respectively, suggest that this measurement has a slight dose dependence. This has been observed in several hydrogen atom reaction studies previously[2,3,5] and is attributed to the background spin-dephasing contributions of second-order spin exchange and recombination reactions between hydrogen atoms and other free radicals in solution. The general expression for the effective damping rate of the FID in these experiments is given by[8]

$$\frac{1}{T_2\,(\text{eff})} = \frac{1}{T_2^{\circ}} + k_s[S] + \sum k_{ex}^{i}[R_i] \tag{4}$$

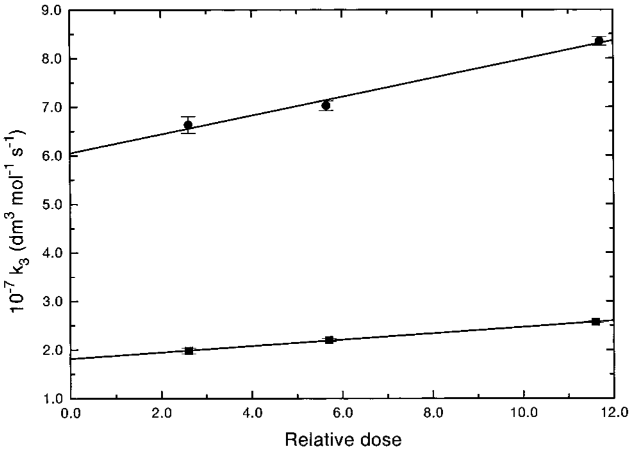

Figure 2. Rate constant extrapolations to zero dose for aqueous hydrogen atom reaction with ethanol at pH 2.0 and 22.0 °C (■) and 61.5 °C (●). Error bars shown correspond to one standard deviation obtained from the linear fit to the FID scavenging plots.

where k_s[S] is the $^{\bullet}$H atom scavenging rate and $\sum k_{ex}^{i}[R_i]$ represents the spin-dephasing contribution of second-order spin exchange and recombination reactions between $^{\bullet}$H atoms and other free radicals. The observed dose dependence occurs when the latter term is not sufficiently constant over the experimental time scale of ca. 5 μs.

To correct the measured rate constants for this dose dependence, limiting values were calculated by extrapolation to zero dose, as shown in Figure 2. An excellent linear relationship was obtained, and for these rate constants a limiting value of (1.83 ± 0.05) × 10^7 dm^3 mol^{-1} s^{-1} was obtained. This procedure was then repeated over the temperature range 6.5−81.3 °C (values for 61.5 °C also shown in Figure 2), with all the extrapolated values given in Table 1 and shown in the Arrhenius plot of Figure 3. Using a ($1/\sigma^2$) weighted linear fit on these values, the temperature-dependent rate constant is well-described by the expression

$$\log_{10} k_3 = (11.53 \pm 0.09) - [(24\,100 \pm 500)/2.303RT] \tag{5}$$

with k_3 and T in units of dm^3 mol^{-1} s^{-1} and K, respectively. This corresponds to an activation energy of 24.1 ± 0.5 kJ mol^{-1}.

There have been many previous determinations, using a variety of techniques, of the rate constant for this reaction.[17,18] Our room temperature (22.0 °C) value of (1.83 ± 0.05) × 10^7 dm^3 mol^{-1} s^{-1} is in very good agreement with the recommended value of 1.7 × 10^7 dm^3 mol^{-1} s^{-1} [18] and at the low end of the range of previous measurements under these experimental conditions, (1.7−4.2) × 10^7 dm^3 mol^{-1} s^{-1}. However, a search of the literature found only one other rate constant determined at another temperature for this reaction. Smaller et al.[14] directly measured a value of 1.3 × 10^7 dm^3 mol^{-1} s^{-1} at 281 K. Our interpolated rate constant of 1.1 × 10^7 dm^3 mol^{-1} s^{-1} is slightly lower than this value but within the combined errors of the two studies.

$^{\bullet}$H with Ethanol-d_5. The use of fully deuterated compounds as standards in steady state competition hydrogen atom rate constant determinations has the advantage that the HD product is readily distinguished by mass spectrometry from the fundamental yield of H_2 produced in water radiolysis. Therefore analogous experiments were performed for hydrogen atom reaction with deuterated ethanol

$$^{\bullet}H + CD_3CD_2OH \rightarrow HD + CD_3{}^{\bullet}CDOH \tag{6}$$

in order to establish the Arrhenius behavior for this compound.

TABLE 1: Summary of the Temperature-Dependent Rate Constant Data for Hydrogen Atom Reaction with Ethanol, Ethanol-d_5, 2-Propanol, and 2-Propanol-d_7 in Aqueous Solution

species	temp, °C	scavenging rate constant, $dm^3\ mol^{-1}\ s^{-1}$
ethanol	6.5	$(1.05 \pm 0.17) \times 10^7$
	13.4	$(1.38 \pm 0.05) \times 10^7$
	22.0	$(1.83 \pm 0.05) \times 10^7$
	30.8	$(2.35 \pm 0.16) \times 10^7$
	41.3	$(3.47 \pm 0.19) \times 10^7$
	61.5	$(5.82 \pm 0.16) \times 10^7$
	70.6	$(7.57 \pm 0.38) \times 10^7$
	81.3	$(9.37 \pm 0.70) \times 10^7$
ethanol-d_5	22.4	$(2.32 \pm 0.22) \times 10^6$
	31.5	$(3.64 \pm 0.13) \times 10^6$
	43.3	$(6.14 \pm 0.38) \times 10^6$
	51.0	$(7.42 \pm 0.70) \times 10^6$
	63.3	$(1.04 \pm 0.09) \times 10^7$
	71.5	$(1.66 \pm 0.42) \times 10^7$
	79.6	$(2.03 \pm 0.21) \times 10^7$
2-propanol	5.4[a]	$(5.95 \pm 0.10) \times 10^7$
	8.8	$(5.92 \pm 0.12) \times 10^7$
	16.5	$(7.23 \pm 0.23) \times 10^7$
	24.7	$(1.02 \pm 0.03) \times 10^8$
	33.7[a]	$(1.33 \pm 0.03) \times 10^8$
	45.5[a]	$(1.80 \pm 0.05) \times 10^8$
	51.0	$(2.35 \pm 0.13) \times 10^8$
	68.0[a]	$(3.00 \pm 0.11) \times 10^8$
	80.3[a]	$(4.29 \pm 0.21) \times 10^8$
	88.5[a]	$(4.98 \pm 0.17) \times 10^8$
2-propanol-d_7	5.7[a]	$(7.08 \pm 0.15) \times 10^6$
	6.6	$(7.42 \pm 0.11) \times 10^6$
	17.2	$(1.10 \pm 0.02) \times 10^7$
	24.7	$(1.51 \pm 0.03) \times 10^7$
	37.6	$(2.41 \pm 0.08) \times 10^7$
	51.2[a]	$(3.48 \pm 0.14) \times 10^7$
	60.0[a]	$(5.07 \pm 0.23) \times 10^7$
	71.8[a]	$(6.84 \pm 0.27) \times 10^7$
	86.5[a]	$(1.12 \pm 0.20) \times 10^8$

[a] pH 4.7.

The dose dependence observed for normal ethanol was also seen for this compound, and rate constants were again extrapolated to zero dose. The value obtained at pH 1.0 and 22.4 °C by this method was $k_6 = (2.32 \pm 0.22) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$, almost 1 order of magnitude slower than the analogous rate constant for ethanol. As this rate constant was close to the lower limit of detection for this experimental system, no measurements were made at lower temperatures, instead rate constants were determined up to 79.6 °C.

The numbers obtained over this range are listed in Table 1 and are plotted in Figure 3. From a weighted linear fit on these values, the temperature-dependent rate constants are well-described by the expression

$$\log_{10} k_6 = (12.03 \pm 0.21) - [(31\,900 \pm 1200)/2.303RT] \tag{7}$$

giving an activation energy of 31.9 ± 1.2 kJ mol^{-1}.

A search of the literature failed to find any previous determination of this rate constant. The rate constant at 22 °C, $k_6 = (2.32 \pm 0.22) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$, is consistent with a single competition-kinetics measurement for hydrogen atom reaction with the analogous compound CH_3CD_2OH, where a rate constant of $6.0 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ at room temperature was obtained.[24] The ratio of the hydrogen atom reaction rate constant with normal ethanol to that for the deuterated compound, $k_H/k_D = 8.8$ observed in this study at room temperature, is in good agreement with the analogous data for reaction with the normal and deuterated acetate ion (17.5),[25,26] formic acid (6.7),[16,27,28] methanol (~25),[5,26] and 2-propanol (8.3).[11,14,29,30] There has only been a single literature report of activation energy differences for hydrogen atom reaction with normal and fully deuterated compounds, where for 2-propanol[31,32] in 6 mol dm^{-3} H_2SO_4 over the temperature range 190−280 K a difference of ca. 4 kJ mol^{-1} was obtained (see later). This isotope effect is somewhat smaller than the experimental difference of 7.8 ± 1.7 kJ mol^{-1} seen in this study for ethanol/ethanol-d_5.

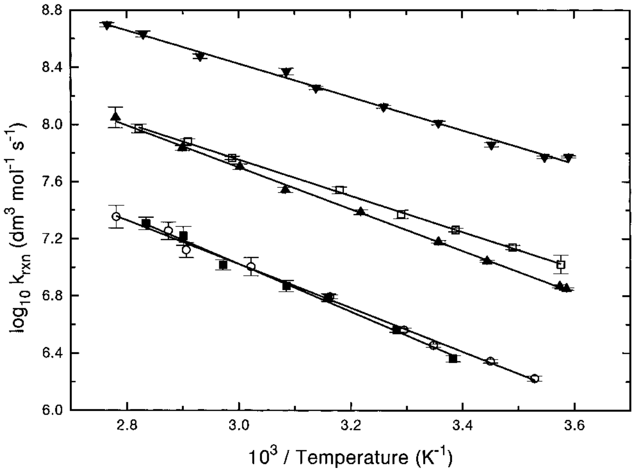

Figure 3. Arrhenius plot of $\log_{10} k_{rxn}$ vs $1/T$ for aqueous hydrogen atom reaction with ethanol (□), ethanol-d_5 (■), 2-propanol (▼), and 2-propanol-d_7 (▲) in comparison to previously obtained values for methanol (○). Solid lines are weighted linear fits, corresponding to activation energies of (24.24 ± 0.29), (31.9 ± 1.2), (22.29 ± 0.59), (28.03 ± 0.44), and (29.37 ± 0.76) kJ mol^{-1}, respectively (see text).

$^\bullet$H Reaction with 2-Propanol. Initial experiments to determine the rate constant for hydrogen atom reaction with 2-propanol

$$^\bullet H + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2{}^\bullet COH \tag{8}$$

showed that the dose dependence observed for ethanol was much smaller for this alcohol, and therefore the reported values in Table 1 are the averages of the individual rate constants at the various pulse widths. Experiments in acidic conditions (<pH 2.0) at elevated temperatures gave rate constants that were far higher than those expected from the extrapolation of lower values in the Arrhenius plot. This acceleration of the reaction rate constant was attributed to the dehydration of the 2-propanol to form the corresponding olefin, $H_2C{=}CHCH_3$, as such behavior has been reported to occur for the lower aliphatic alcohols in the presence of dilute acid solutions (although at much higher temperatures), and to be catalyzed by the presence of certain metals such as nickel.[33] This unsaturated product would be expected to react at a far faster rate than the alcohol, leading to an increase in the observed rate constant. Therefore to obtain accurate hydrogen atom reaction rate constants for only 2-propanol at higher temperatures, (5−10) × 10^{-3} mol dm^{-3} phosphate buffer was added to keep the pH ~5 and FID traces were obtained using the 55 ns pulse width. Rate constants obtained at lower temperatures using this method were found to be in excellent agreement with the values measured in acidic solution.

The Arrhenius plot for reaction 8 is also shown in Figure 3 and over the temperature range 5.4−88.5 °C is well-described by the equation

$$\log_{10} k_8 = (11.86 \pm 0.05) - [(22\,000 \pm 260)/2.303RT] \tag{9}$$

The activation energy of 22.00 ± 0.26 kJ mol^{-1} is slightly lower than the value for ethanol, consistent with the formation of the more stable radical product. The room temperature (22.0 °C) calculated value is $k_8 = (9.34 \pm 0.07) \times 10^7$ dm^3 mol^{-1} s^{-1}, slightly higher than the recommended value of 7.4×10^7 dm^3 mol^{-1} s^{-1}.[18] This measured rate constant is in excellent agreement with a previous determination of $(9.0 \pm 2.0) \times 10^7$ dm^3 mol^{-1} s^{-1} using this EPR technique[6] but at the low end of the range of the previous determinations under these conditions, $(6.5-17) \times 10^7$ dm^3 mol^{-1} s^{-1}.[17,18]

There has been one previous investigation of the temperature dependence of this reaction, where in 6 mol dm^{-3} H_2SO_4 over the temperature range 190−280 K an activation energy of 16 ± 2 kJ mol^{-1} was found.[31] The Arrhenius behavior of all the rate constants was given by

$$\log_{10} k = (11.0 \pm 0.1) - [(16\,000 \pm 2000)/2.303RT] \quad (10)$$

For the one overlapping temperature point of the two studies, $T = 5.4$ °C, our rate constant, $k_8 = (5.95 \pm 0.10) \times 10^7$ dm^3 mol^{-1} s^{-1}, is within the (relatively large) error of their calculated value of ca. 1.0×10^8 dm^3 mol^{-1} s^{-1}.

$^{\bullet}$H Reaction with 2-Propanol-d_7. Identical experiments were also performed for deuterated 2-propanol,

$$^{\bullet}\mathrm{H} + (\mathrm{CD}_3)_2\mathrm{CDOH} \rightarrow \mathrm{HD} + (\mathrm{CD}_3)^{\bullet}\mathrm{COH} \quad (11)$$

and again the apparent acceleration of the rate constant in acidic media at higher temperatures necessitated the use of phosphate buffers. The measured temperature-dependent rate constants are summarized in Table 1 and shown in the Arrhenius plot of Figure 3. For this alcohol, the rate constants are described by the expression

$$\log_{10} k_{11} = (12.00 \pm 0.06) - [(27\,450 \pm 300)/2.303RT] \quad (12)$$

essentially having the same pre-exponential factor as 2-propanol but with an activation energy higher by 4.75 kJ mol^{-1}.

The reaction in 6 mol dm^{-3} H_2SO_4 solution has also been performed,[32] as for 2-propanol, over the temperature range 77−273 K. Specific rate constants were determined for the abstraction of D, reaction 11 ($\log_{10} k = (10.80 \pm 0.03) - [(20\,000 \pm 2600)/2.303RT]$), and also for the abstraction of the hydroxylic H atom

$$^{\bullet}\mathrm{H} + (\mathrm{CD}_3)_2\mathrm{CDOH} \rightarrow \mathrm{H}_2 + (\mathrm{CD}_3)_2\mathrm{CDO}^{\bullet} \quad (13)$$

($\log_{10} k = (10.40 \pm 0.09) - [(23\,000 \pm 3000)/2.303RT]$), respectively. These expressions indicate that over the temperature range of our study (5−88 °C) reaction 11 would dominate. The slight extrapolation of the results of ref 32 to $T = 5.7$ °C gives $(1.1 \pm 0.7) \times 10^7$ dm^3 mol^{-1} s^{-1}, which is slightly higher than, but within range of, our measured value of $k_{11} = (7.08 \pm 0.15) \times 10^6$ dm^3 mol^{-1} s^{-1}.

4. Discussion

The comparison of the new measurements for ethanol with the previous results for methanol[5] provides an interesting contrast. The Arrhenius plot for hydrogen atom reaction with methanol is also shown in Figure 3 and is noted to have a higher activation energy (29.4 vs 24.1 kJ mol^{-1}) but essentially the same pre-exponential factor as ethanol. For methanol, the room temperature gas phase rate constant[34] of 2.3×10^6 dm^3 mol^{-1} s^{-1} is virtually identical to the aqueous phase value of 2.84×10^6 dm^3 mol^{-1} s^{-1}, although the liquid phase activation energy is 6.5 kJ mol^{-1} larger than the gas phase result.[34] The hydrogen atom gas phase reaction rate constant for ethanol has been determined over the temperature range 295−700 K[35] with values described by the equation

$$\log_{10} k_{3,\mathrm{g}} = (9.62 \pm 0.04) - [(17\,600 \pm 1200)/2.303RT] \quad (14)$$

At 22 °C, the calculated gas phase rate constant is 3.25×10^6 dm^3 mol^{-1} s^{-1}, about a factor of 3 slower than that observed in this solution study. The gas phase activation energy of 17.6 ± 1.2 kJ mol^{-1}, however, is again approximately 6.5 kJ mol^{-1} lower than that observed in the liquid phase.

TABLE 2: Activation Entropy and Enthalpy Contributions from ab Initio HF/6-31G* Calculations

contribution/ alcohol	electronic (kJ mol^{-1})	zero-point energy (kJ mol^{-1})	v,r,t enthalpy (kJ mol^{-1})	v,r,t entropy (J K^{-1} mol^{-1})
methanol	95.37	−7.37	−5.99	−96.86
methanol-d_3	95.37	−2.19	−0.58	−97.07
isotope effect	0	−5.18	−5.41	+0.21
ethanol	88.53	−7.86	−5.92	−96.36
ethanol-d_5	88.53	−2.48	−0.48	−96.19
isotope effect	0	−5.38	−5.44	−0.17
2-propanol	82.84	−7.79	−5.62	−95.94
2-propanol-d_7	82.84	−2.42	−0.23	−95.54
isotope effect	0	−5.37	−5.39	−0.40

In order to assess the source of these solvent effects and the measured isotope effects, ab initio calculations of $^{\bullet}$H and $^{\bullet}$D abstraction from the protonated and deuterated methanol, ethanol, and 2-propanol were carried out at the Hartree−Fock level with 6-31G* basis set. Vibrational analysis of both the transition state and reactants allows calculation of the activation enthalpies and entropies and the isotope effect, with the aid of the standard transition state expression[36]

$$k_{\mathrm{react}} = \frac{kT}{h} \mathrm{e}^{(\Delta S^{\ddagger}/R)} \mathrm{e}^{-(\Delta H^{\ddagger}/RT)} \quad (15)$$

where k is the Boltzmann constant, h is the Planck constant, and the transmission coefficient has been assumed to be unity. This level of theory is insufficient to give accurate electronic activation energies (the barriers are far too high), but the comparison of isotope effects for the three molecules should give a reasonable qualitative picture for the gas phase reactions in the absence of tunneling. The effects on internal vibrational frequencies should be similar in water. Tunneling effects in the $^{\bullet}$H abstraction reactions are known to be important in the gas phase,[37−39] but it has also been shown that tunneling may be substantially quenched in the aqueous environment.[40]

Results of the calculations are tabulated in Table 2. It can be seen that the activation entropy in these calculations has only a weak dependence on isotopic substitution and roughly the same value for all six molecules. Consequently the Arrhenius pre-exponential factor should be nearly the same for the six molecules, just as observed in water. Total activation enthalpy includes translational, rotational, and vibrational contributions as well as electronic and vibrational zero-point energy. The major isotope effect on the activation enthalpy reflects the difference in vibrational zero-point energies, and the isotope effect is nearly the same for all three alcohols.

Not indicated in Table 2 is the difference in dipole moments between the three ground state alcohols and the corresponding transition states, which amount to a decrease of several tenths of a debye. The Kirkwood formula[36] for solvation of a dipole in a dielectric continuum is (in atomic units)

$$\Delta G_{\mathrm{solv}} = -\frac{\mu^2}{b^3}\frac{(\epsilon - 1)}{(2\epsilon + 1)} \qquad (16)$$

where μ is the dipole moment, b is the molecular radius, and ϵ is the dielectric constant. Given the large dielectric constant of water, the change in dipole moment could add several kJ mol^{-1} to the aqueous barrier height over the gas phase value. This does not account for the much larger pre-exponential factors in the liquid, however. In previous work on benzene,[7] it was demonstrated that aqueous rate constants for $^{\bullet}$H atom addition could be enhanced by factors of 35−40 by virtue of the hydrophobic nature of the $^{\bullet}$H atom. This "hydrophobic attraction" must also account for most of the positive entropy contribution required to enhance the pre-exponential factor over the gas phase value in these abstraction reactions.

5. Conclusion

Arrhenius parameters have been established for aqueous hydrogen atom reaction with ethanol, ethanol-d_5, 2-propanol, and 2-propanol-d_7 by direct experimental measurement as

$$\log_{10} k_3 = (11.53 \pm 0.09) - [(24\,100 \pm 500)/2.303RT] \qquad (5)$$

$$\log_{10} k_6 = (12.03 \pm 0.21) - [(31\,900 \pm 1200)/2.303RT] \qquad (7)$$

$$\log_{10} k_8 = (11.86 \pm 0.05) - [(22\,000 \pm 260)/2.303RT] \qquad (9)$$

and

$$\log_{10} k_{11} = (12.00 \pm 0.06) - [(27\,450 \pm 300)/2.303RT] \qquad (12)$$

respectively. To within the stated error, the room temperature rate constants of this study agree with the recommended values of ref 18, thus confirming the rate constants of that review which were obtained by competition with these alcohols. Because the relative rates obtained in the competition studies are often very precise, significant reduction in the uncertainties of many rate constants previously determined by competition should now be possible. The rate constants derived in the present study will also make competition experiments possible at other temperatures, although we have also demonstrated that use of 2-propanol at elevated temperatures requires some caution.

Ab initio calculations performed for these abstraction reactions showed that the major isotope effect occurs in the activation enthalpy, but that this effect was nearly the same for methanol, ethanol, and 2-propanol, consistent with the experimental observations. Comparison with limited gas phase data suggests that the "hydrophobic attraction" of $^{\bullet}$H to the alcohol enhances the pre-exponential factors.

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